

US EPA ARCHIVE DOCUMENT

***Compact multi-pollutant mid-IR laser  
spectroscopic trace-gas sensor  
towards applications in distributed wireless sensor networks***

Gerard Wysocki

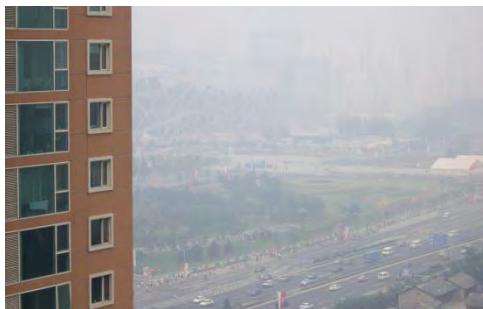
Andreas Hangauer, Clinton Smith,  
Stephen So<sup>#</sup>, Oscar Li

Princeton University Electrical Engineering Dept., Princeton NJ 08544

<sup>#</sup> Sentinel Photonics, Monmouth Junction, NJ 08852 USA



**Environmental Monitoring**



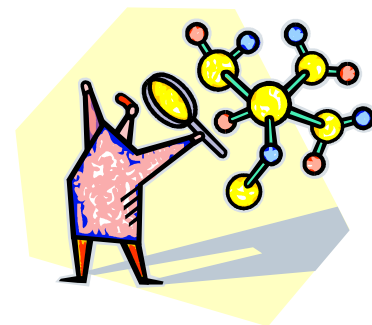
**Urban and Industrial Emission Measurements**

**Remote sensing and Space exploration**



**Industrial Process Control**

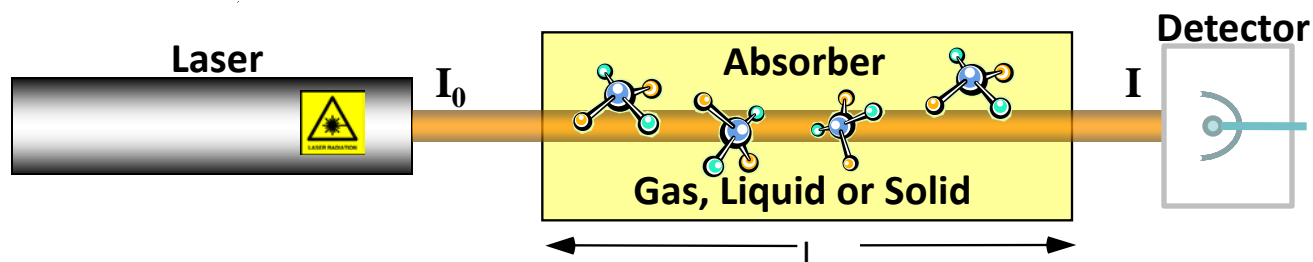
**Fundamental Science**



**Law Enforcement and National Security**

- Sensing of airborne chemicals is of importance in a number of atmospheric monitoring applications and will play a major role in further improvement of emissions inventories
- Recent studies indicate that industrial emissions may be 10-20x greater than the amount estimated using current standard emission factors
- Development of new, sensitive, multi-species sensing technologies, which can be configured into wireless sensor networks (WSNs) to create dynamic pollutant concentration maps will be a critical step towards improvement of the emission control and monitoring

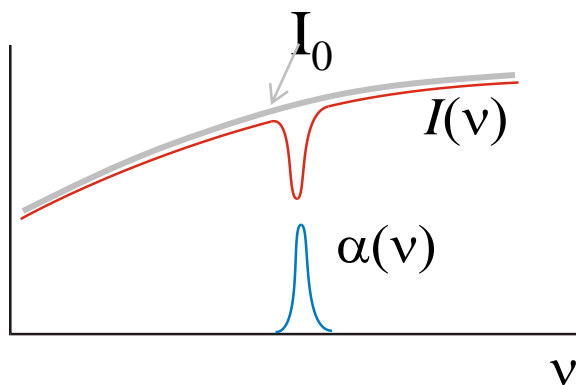
- High sensitivity
- High selectivity
- Non-destructive
- Fast
- No sample preparation
- Remote sensing
- Field deployable



## Beer-Lambert's Law of Linear Absorption

$$I = I_0 \cdot e^{-\alpha(\nu) \cdot L}$$

$\alpha(\nu)$  - absorption coefficient [ $\text{cm}^{-1}$ ];  $L$  - path length [ $\text{cm}$ ]  
 $\nu$  - frequency [ $\text{cm}^{-1}$ ];



$$\alpha(\nu) = S(T) \cdot g(\nu - \nu_0) \cdot N$$

$N$  - concentration [ $\text{molecule} \cdot \text{cm}^{-3}$ ]

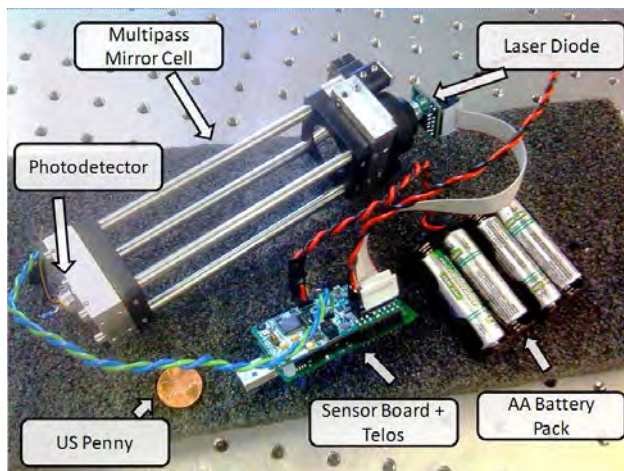
$S$  - molecular line intensity [ $\text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$ ]

$g(\nu - \nu_0)$  - normalized lineshape function [ $\text{cm}$ ], (Gaussian, Lorentzian, Voigt)

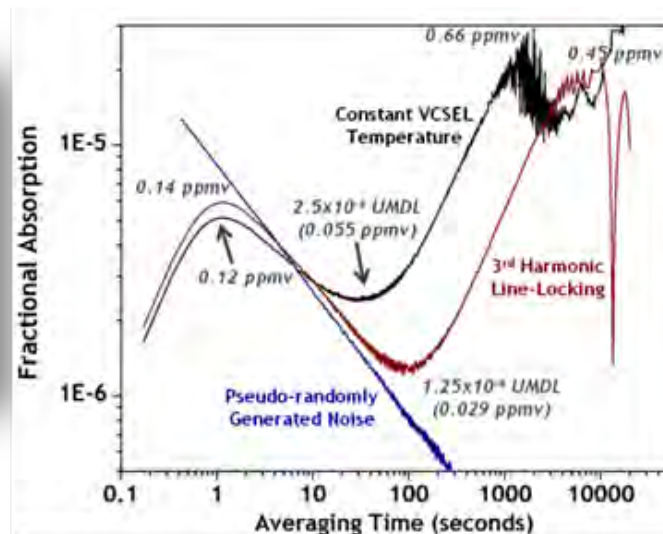
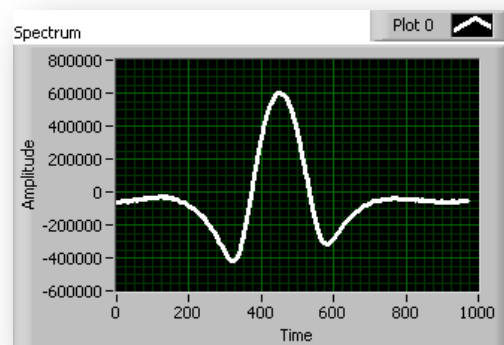
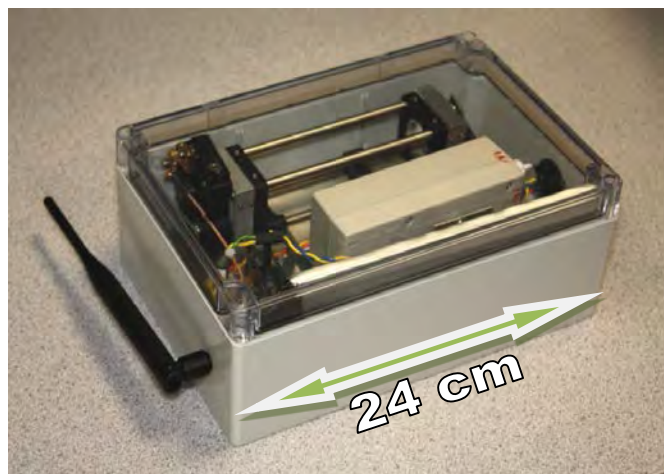
- Semiconductor lasers used as spectroscopic sources can yield compact, sensitive and selective spectroscopic trace-gas sensors
- We have developed a ultra-low-power embedded laser spectroscopic sensor systems employing telecommunication diode lasers for atmospheric CO<sub>2</sub> monitoring
- Modular expansion design allows for flexibility in configuration for specific applications as well as for efficient adoption of new laser technologies



# Demo of CO<sub>2</sub> Sensor @ 2 microns

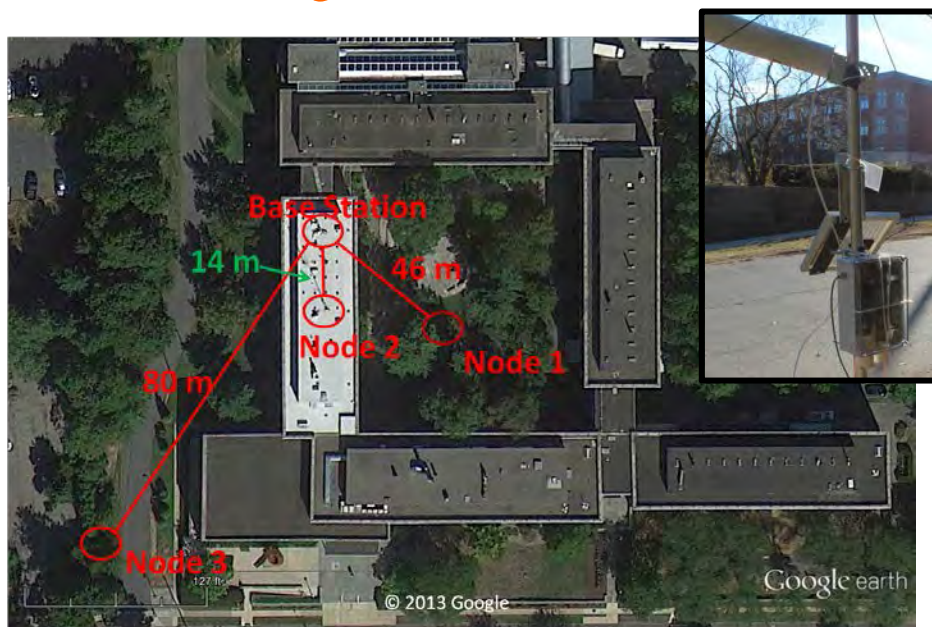


- Fully autonomous, fully digital
- ~0.3W total consumption (continuous) w/ wireless transmission
- >16 Hour run time on NiMH AA batteries (continuous)
- CO<sub>2</sub> sensor node:
  - Sensitivity ~**120ppb in 1sec.**
  - 3.5 meter multipass cell

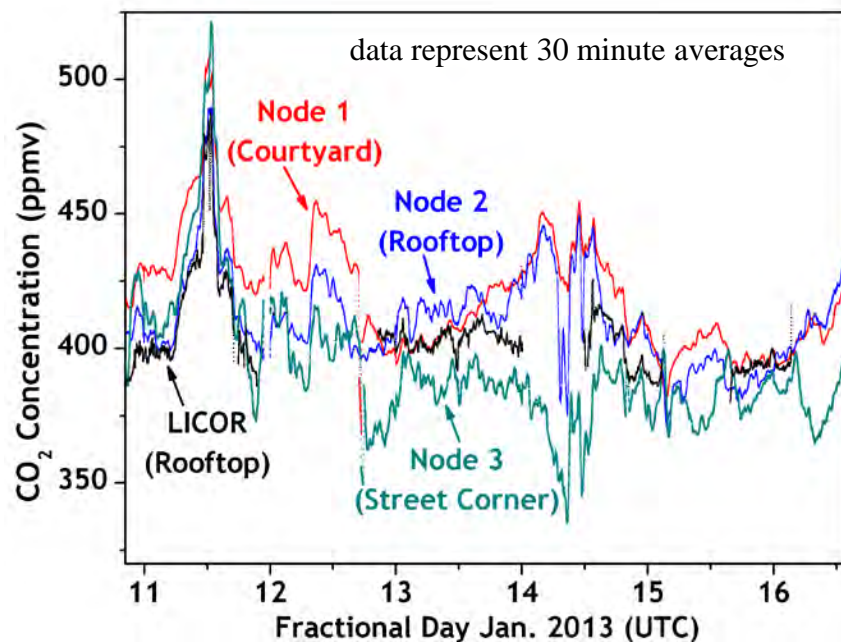




## Laser spectroscopic WSN for CO<sub>2</sub> monitoring around the E-QUAD at Princeton University



Data from the WSN shown with the commercial CO<sub>2</sub> analyzer available on site



- Time-division-multiple-access network (TDMA) scheme based on commercial wireless communications cards coupled with the sensor electronics via UART
- Nodes 1 and 3 were solar-powered during the entire deployment.
- The sensors show consistent results and the network interaction is virtually transparent.

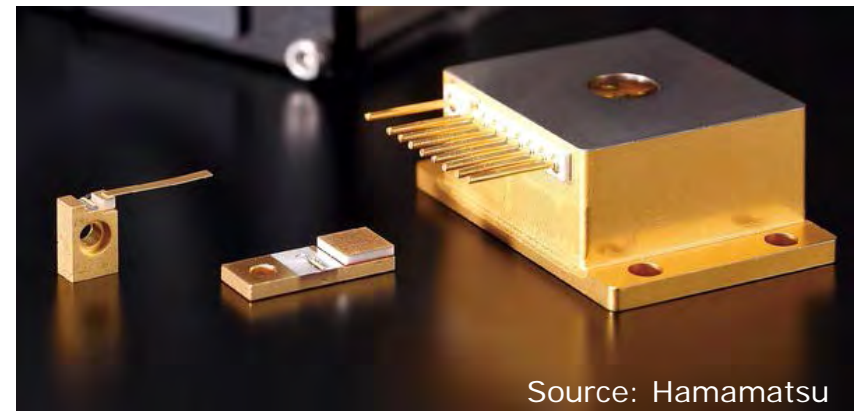
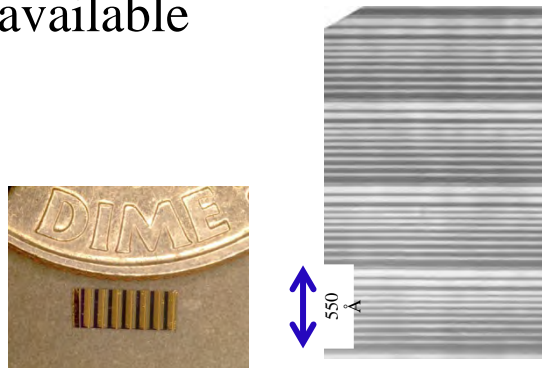
- Most chemical compounds in gas phase (including volatile organic compounds, or hydrocarbons) have their strongest fundamental ro-vibrational transitions in the mid-infrared region ( $\sim 3\text{-}16\ \mu\text{m}$ ).
- To perform spectroscopic multi-component analysis of chemical species, widely tunable mid-IR laser sources are needed
- Similarly spectroscopic instrumentation that is capable of identification and quantification of large molecular compounds with broadband spectral signatures (e.g. VOCs and other environmentally important molecules) require wide spectral tuning

### **Therefore:**

- Mid-IR spectroscopy and spectroscopic WSNs can greatly benefit from the development and implementation of new widely tunable laser sources for multi-component chemical analysis

# Quantum Cascade Lasers: Basic Facts

- Laser wavelengths in the Mid-IR range : ( $\sim 3 - 24\mu\text{m}$ , band structure engineering)
- High laser power : ( $>500\text{mW}$  cw,  $>5\text{W}$  peak for pulsed)
- Tunable single frequency operation (DFB up to  $\sim 10\text{ cm}^{-1}$ , EC  $>300\text{ cm}^{-1}$ )
- Linewidth ( $<0.001\text{ cm}^{-1}$  for CW and  $<0.03\text{ cm}^{-1}$  for pulsed)  
(Cascading: 1 electron = N photons; WPE  $\sim 50\%$  recently reported)
- High reliability, long lifetime
- Room temperature operation : (CW: above RT)
- Compact
- Commercially available



- Develop a sensor node with WSN capabilities for detection of multiple trace-gas pollutants

## **Specific tasks:**

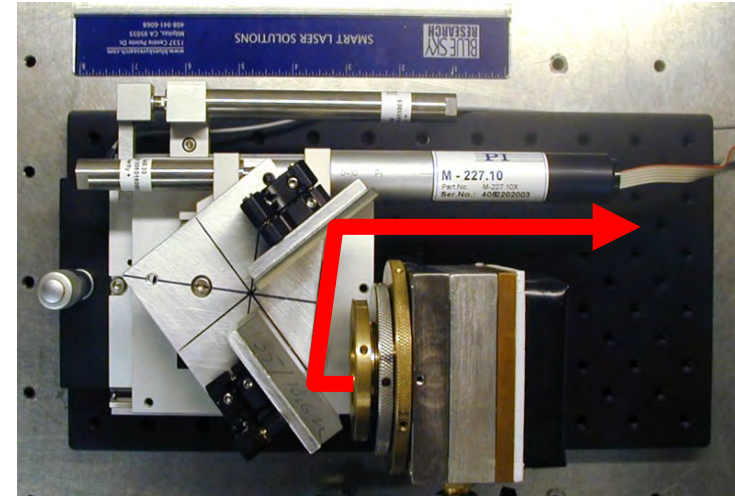
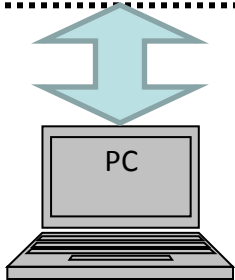
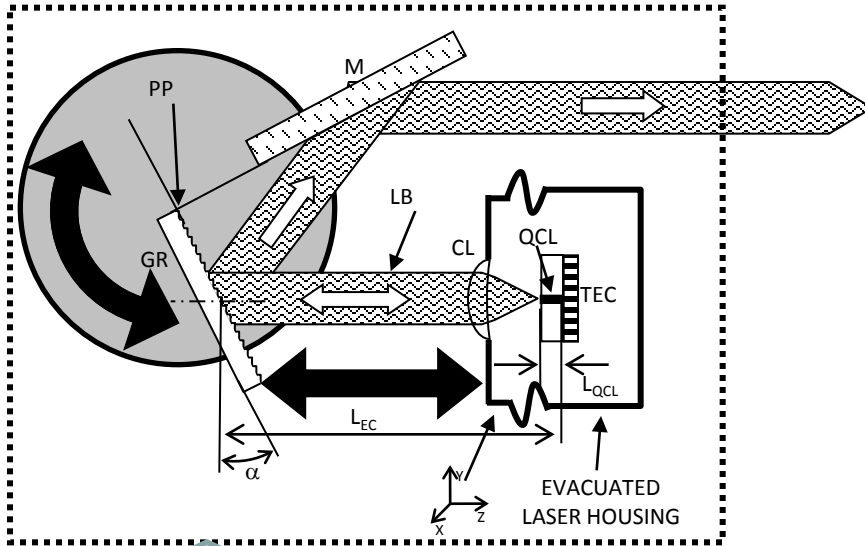
- Adopt widely tunable quantum cascade laser technology for spectroscopy of broadband absorbers



- Build a proof-of-concept prototype spectrometer targeting Benzene ( $\text{C}_6\text{H}_6$ ) and Ammonia ( $\text{NH}_3$ ) to demonstrate multi-species detection



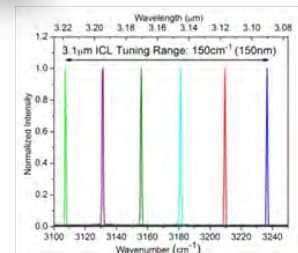
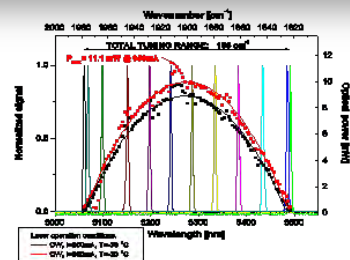
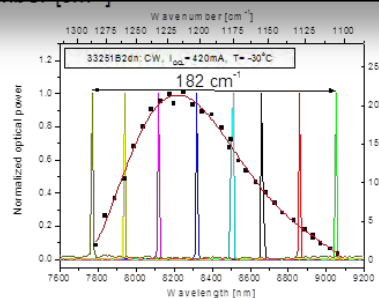
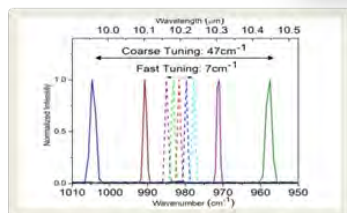
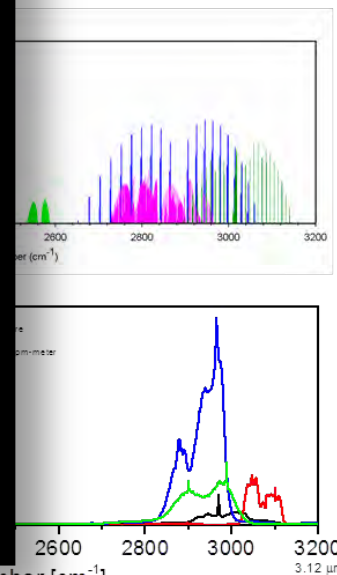
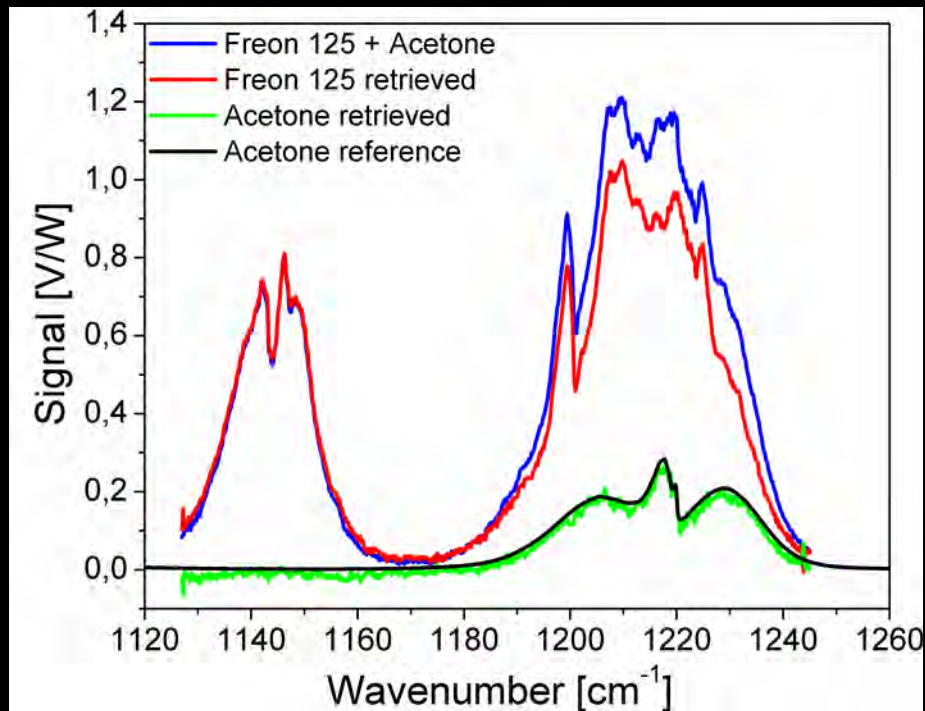
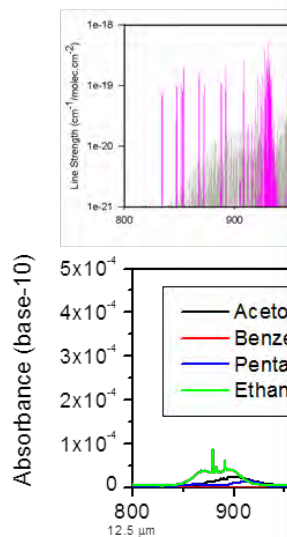
- Perform instrument field test and inter-comparison with other established technologies



- High resolution mode-hop free wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning

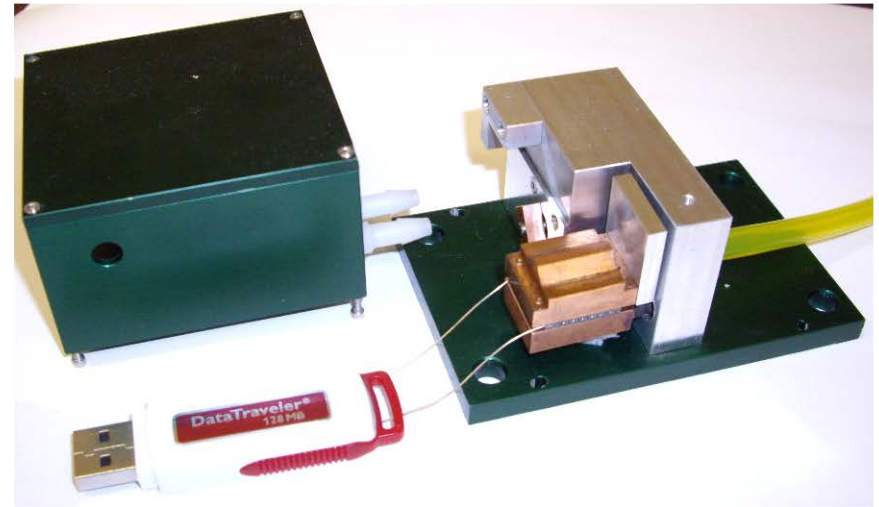
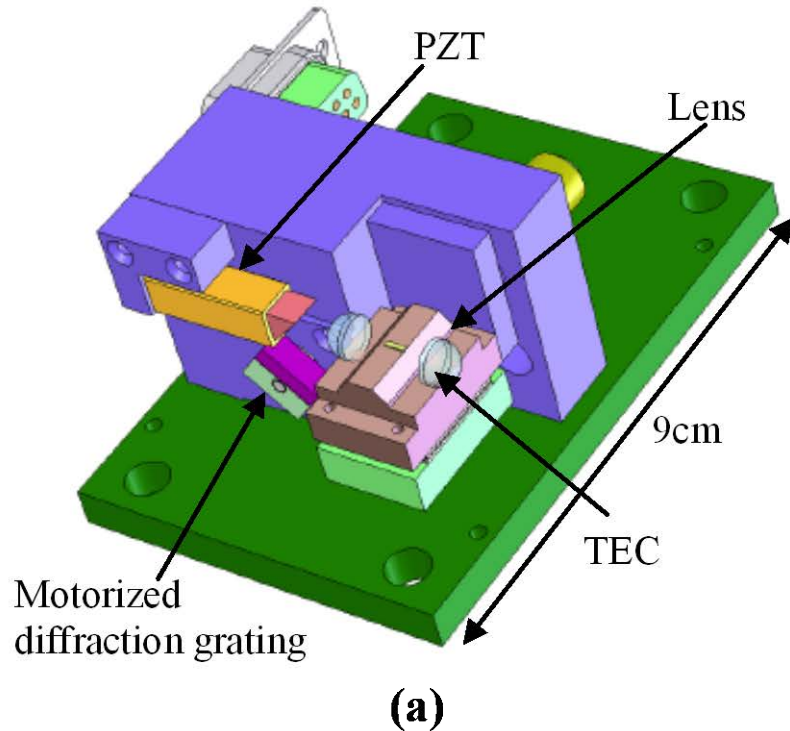


Atmospheric  
absorption  
(100m open pa



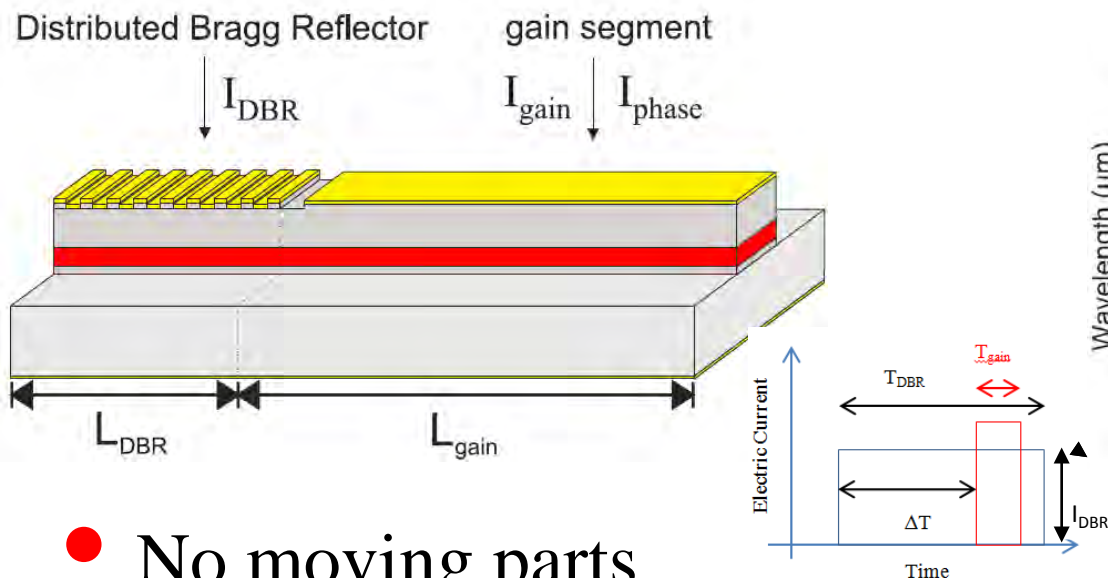


## Miniature EC-QCL

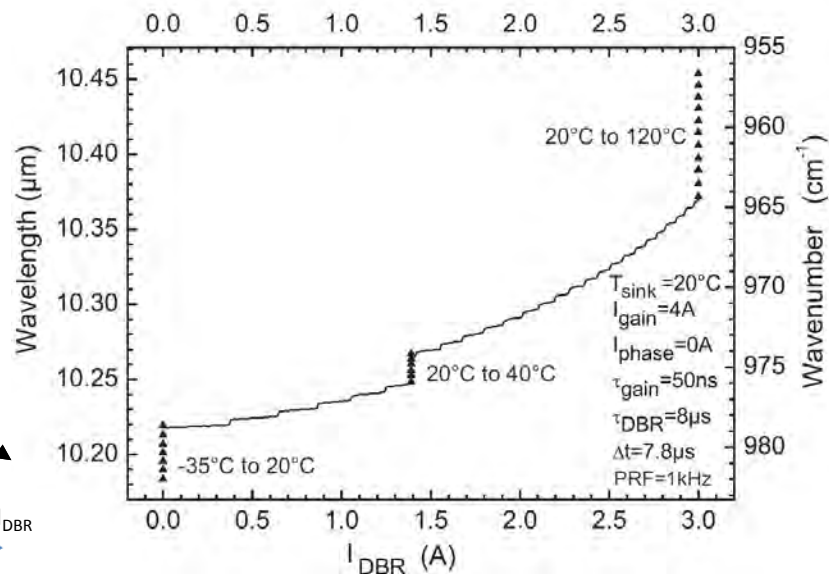


- High efficiency thermal management
- Integrated micro-aligned optics
- >200ml total size of the laser head
- High mechanical and thermal stability

## Distributed Bragg grating QCL Schematic



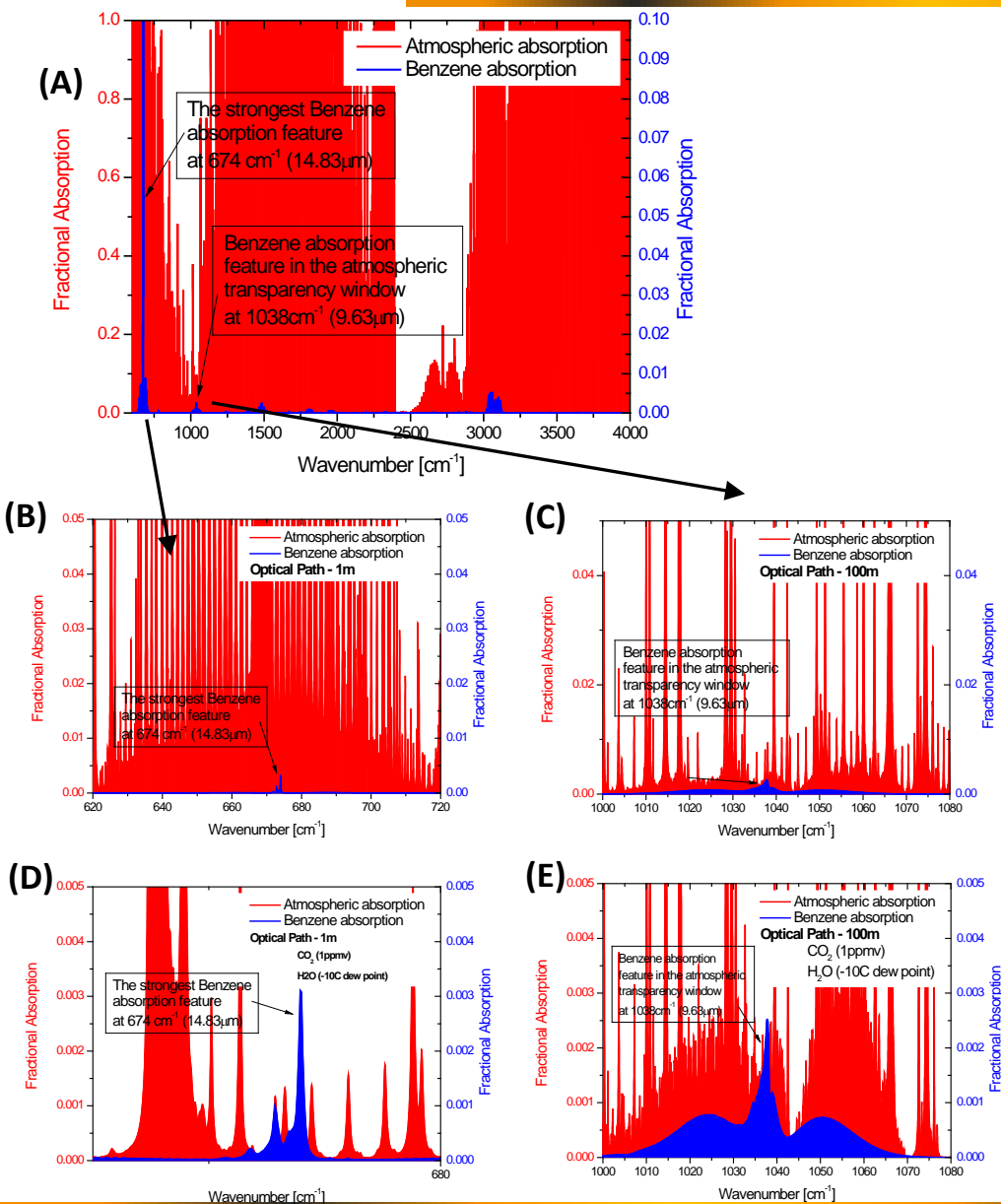
## Tuning range



- No moving parts
  - Excellent opto-mechanical stability
  - Ideal for field deployments
- Fully electrical broadband tuning
  - Gain current tuning: narrow, continuous
  - DBR current tuning: wide, discrete (controlled longitudinal mode hopping)

Source: P. Fuchs, et. al, Opt. Express **20**, 3890-3897 (2012).

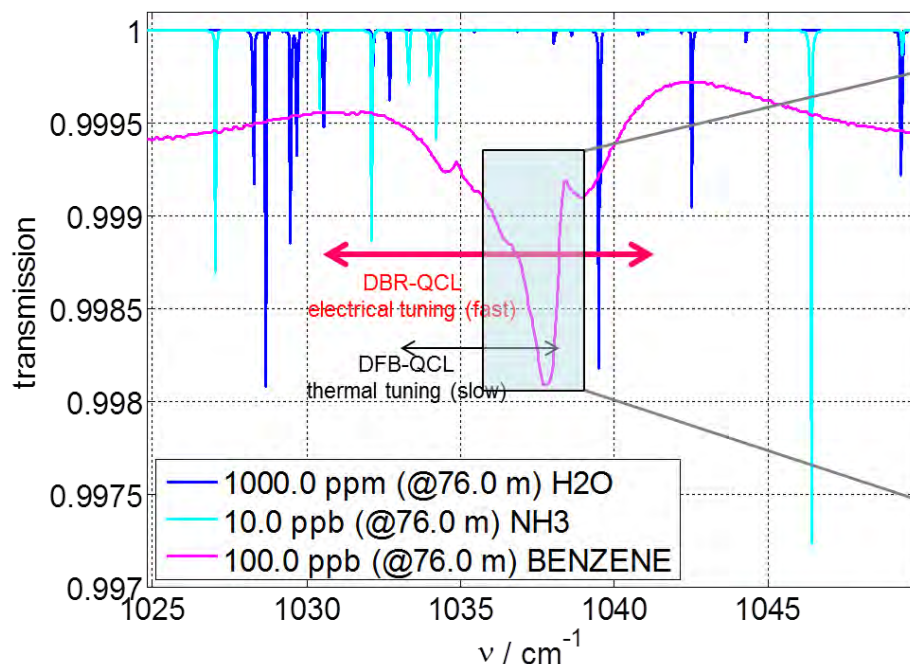
Parameters	External Cavity EC-QCL	Distributed Bragg Grating DBR-QCL	Distributed feedback DFB-QCL
Maximum Tunability	up to 400cm <sup>-1</sup>	~10cm <sup>-1</sup> (electrical); >20cm <sup>-1</sup> (thermal)	1-2cm <sup>-1</sup> (electrical); ~10cm <sup>-1</sup> (thermal)
Scan repetition rate	Slow (<100Hz)	Fast (10-100kHz) (thermal- slow)	Fast (10-100kHz) (thermal- slow)
Construction / tuning	Moving parts / Opto- mechanical	No moving parts / electrical	No moving parts / electrical



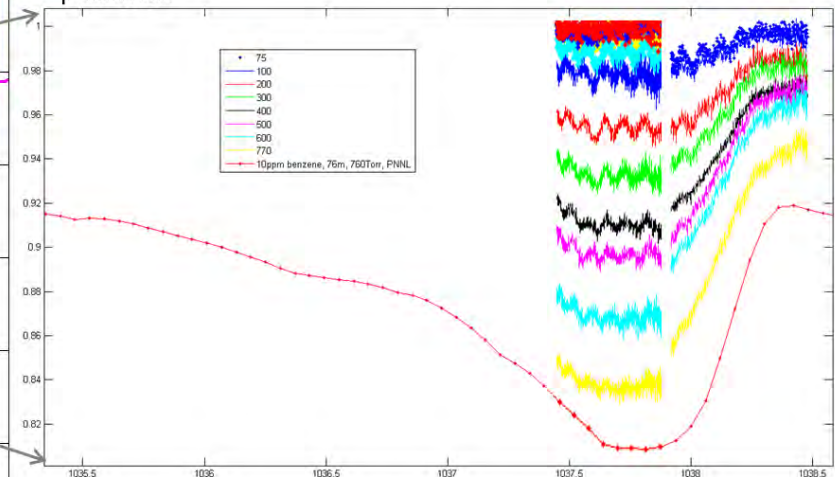
- (A) Absorption features of 100ppb Benzene (blue) over 100m optical path plotted together with average atmospheric absorption (red).
- (B) The strongest absorption band of Benzene (blue) and the atmospheric interference (red) calculated for 1m optical path
- (C) The absorption band of Benzene (blue) at 9.63 $\mu m$  and the atmospheric interference (red) calculated for 100m optical path
- (D) and (E) pre-conditioned air sample with  $CO_2$  scrubbed to 1ppmv level and moisture removed down to -10 $^{\circ}C$  dew point.

# Preliminary spectroscopy of $C_6H_6$ at $9.6\mu m$

Transmission spectrum of a mixture of  $C_6H_6$ ,  $NH_3$ , and  $H_2O$  in  $N_2$



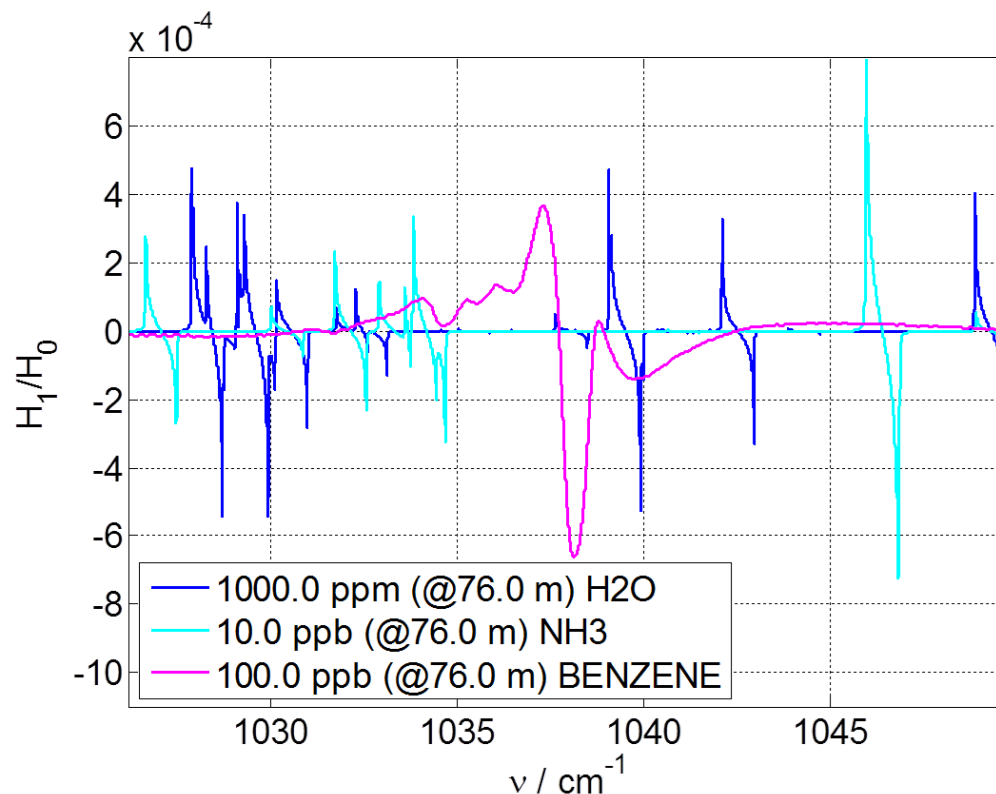
Transmission spectrum of 10ppm  $C_6H_6$  in  $N_2$  acquired at different pressures



- Spectral simulations of the  $C_6H_6$  band at  $9.6\mu m$ 
  - The entire feature spans  $\sim 50 cm^{-1}$
  - The Q-branch at  $1037 cm^{-1}$  is narrow ( $\sim 3 cm^{-1}$ ) and shows relatively small interference from other species
- Preliminary transmission data collected using a DFB-QCL operating at  $1037 cm^{-1}$
- The  $5 cm^{-1}$  thermal tuning range of a DFB QCL gives access to both species ( $C_6H_6$  and  $NH_3$ ) and could be used for detection
- **DBR-QCL with  $>10 cm^{-1}$  fast electrical tuning – best for trace-gas WSN-node**



# Simulation of wavelength modulated spectra of $C_6H_6$ at $9.6\mu m$



- Wavelength modulation spectroscopy (WMS) shifts the demodulated spectroscopic signal to higher frequencies
- Reduction of the  $1/f$  noise and smaller detection bandwidth than in direct-LAS will result in higher sensitivity
- A DFB-QCL current modulation amplitude of  $\sim 54$  mA provides optimum ( $\sim 0.5\text{cm}^{-1}$ ) modulation depth



- The spectroscopic WSN platform has been tested in the field and showed results consistent with other commercial sensors
- Preliminary spectroscopy of  $\text{C}_6\text{H}_6$  with DFB-QCL has been performed
- DBR-QCL technology has been identified as the most promising broadband mid-IR source for WSN applications
- DBR-QCL is currently under test in our laboratory

- **Dr. Johannes Koeth** at Nanoplus GmbH for providing DBR-QCL for this study



Funding:

- **EPA STAR Program**
- **NSF ERC MIRTHE**
- **NSF MRI program**

